PVC Paste Rheology: Polymer Properties and Viscoelastic Behaviour

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Considering the several types of poly(ethylene) and poly(vinyl chloride) (PVC), PVC is the second world consumed thermoplastic. Although the vast majority of homopolymer and copolymer products are produced in a suspension system, a particular type is produced by the emulsion or microsuspension processes, making the so called dispersion grades (Saeki and Emura, 2002). These types of PVC polymers are normally fine powders of spherical particles (0.1-15 μm) that are mixed with a plasticizer to produce a dispersion (suspension), normally referred as paste or plastisol. Industrially, the said dispersion is applied over a substrate, by spreading, coating or molding, before the gelification and fusion into the final commercial products, such as: films, sheets, paper coatings, mats, flooring, life preservers and roof tops (Sarvetnick, 1972; Nakajima and Harrel, 2001).

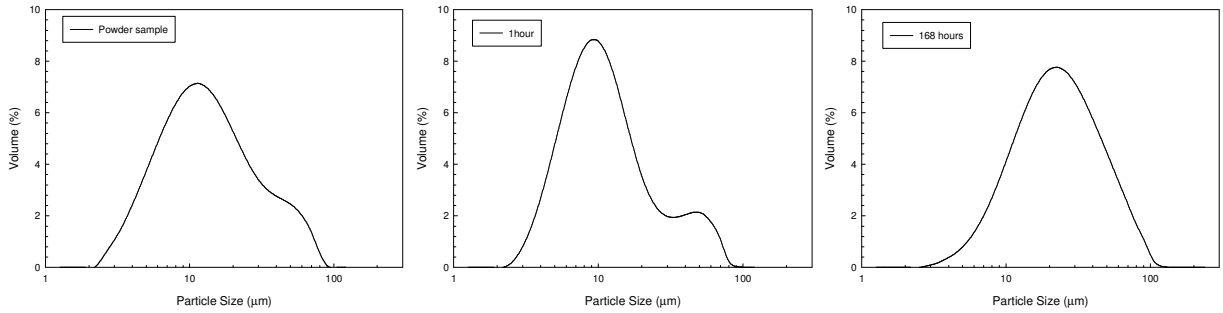
Depending on each application type, the shear stress applied over the plastisol during the production stage makes the study of the paste's rheological behaviour a very important factor to determine and fine tune all process conditions and formulations (Marcilla *et al*, 1997). Also, in the particular case of the emulsion PVC polymers, the conditions during the free radical polymerization, as well as the process conditions of the industrial spray-dryer and subsequent milling of the powder, can have a great influence over the final properties (Nakajima and Harrel, 2001).

The emulsion polymers are normally made up in the presence of a surfactant and a free radical initiator, to produce a polymer that can have different particle sizes and surface characteristics. Also, depending on the production process, an aggregation effect is normally observed, affecting the size and size distribution of the final powder. Nevertheless, during the plastisol formation, these agglomerated particles are not sufficiently strong to resist to the high shearing mixing conditions, together with the solvating plasticizer effect over the polymer. This effect is normally translated by an increase of the plastisol viscosity with time, in a process normally called "viscosity aging" (Nakajima and Harrel, 2005). The aging rate and the rheological behaviour of the plastisols are also sensitive to the type of surfactants used during the polymerization process, type and quantity of plasticizer and to other additives used in the final formulation, such as fillers, pigments and thermal stabilizers (Sarvetnick, 1972, Alsopp and Vianello, 2003).

The application of a developed laser diffraction spectroscopy's technique (LDS) to evaluate the particle size distribution of the initial polymer's powder, as well as his evolution on the plastisols, allows very significant information of the aggregates dimension during the aging period, correlating with the paste's viscoelastic response (Rasteiro and Antunes, 2005) . This relationship, together with the auxiliary analysis of the zeta potential, fractal dimension and morphological observations of the powder, can contribute for a better understanding of all parameters affecting the overall rheological behaviour.

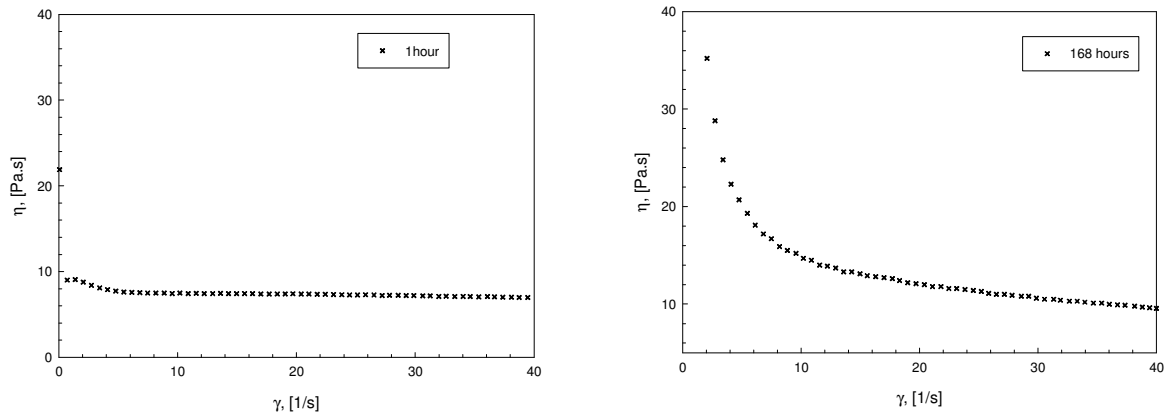
Although less studied, the intrinsic properties of the emulsion polymers, such as molecular weight distribution and thermal stability, which are closely related with the polymerization's conditions, can provide a valuable insight to tune and/or modify the production process, namely, the selection of surfactants and the type of free radical initiator used in several reaction steps of a common semi-batch industrial reactor.

On figure 1, the PSD evolution from the original powder to a given plastisol formulation, since it was prepared (1h) until 24h after, clearly demonstrates the aggregates destruction over time and the correspondent modifications on the newtonian viscosity (figure 2 a), b)).



a) Powder b) Plastisol 1h c) Plastisol 168hours

Figure 1: PSD distributions (from LDS) of powder sample (a), plastisol sample at 1h (b) to 168h (c).



a) Plastisol at 1h b) Plastisol at 168h

Figure 2: Viscosity (η) *vs* shear rate (γ) for plastisol sample at 1h (a) and 168h (b).

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